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OFFICE OF NAVAL RESEARCH

PROGRAM ELEMENT 61153N

TECHNICAL REPORT NO. 6

NRL BORON PROPELLANTS COMBUSTION PROGRAM

BY

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Published

in the

Proceedings of the 1988 AFOSR/ONR

Contractor's Meeting on Combustion

15-19 June 1988, Los Angeles, CA

CHEMISTRY DIVISION

NAVAL RESEARCH LABORATORY

WASHINGTON, DC 20375-5000

JUNE 1988

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS NONE
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Naval Research Laboratory 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Chemistry Division Office of the Chief of Naval Research
6c. ADDRESS (City, State, and ZIP Code) Washington, DC 20375-5000	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 61153N; PROJECT NO. RR013-01-4C; TASK NO.; WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) NRL Boron Propellants Combustion Program(U)	
12. PERSONAL AUTHOR(S) H.H. Nelson	
13a. TYPE OF REPORT 13b. TIME COVERED FROM 9/87 TO 9/88	14. DATE OF REPORT (Year, Month, Day) JUNE 1988 15. PAGE COUNT
16. SUPPLEMENTARY NOTATION	

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The NRL program on High-Energy Propellant Chemistry includes work in three project areas. The first of these is a mass spectrometry based study of the oxide layer formed at the surface of elemental boron. The second involves the study of chemical mechanisms of homogeneous boron combustion. This work has focussed on boron hydrides in the past year but is expanding to cover boron oxyhydrides. The third area is a theoretical investigation of important intermediates in boron combustion. Structures, thermodynamics and reaction pathways are being studied. All three projects are oriented to assist in the understanding and control of heterogeneous and homogeneous combustion of boron and boron-doped fuels.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL J.R. McDonald	22b. TELEPHONE (Include Area Code) (202) 767-3340 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

NRL BORON PROPELLANTS COMBUSTION PROGRAM

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SUMMARY/OVERVIEW:

The NRL program on High-Energy Propellant Chemistry includes work in three project areas. The first of these is a mass spectrometry based study of the oxide layer formed at the surface of elemental boron. The second involves the study of chemical mechanisms of homogeneous boron combustion. This work has focussed on boron hydrides in the past year but is expanding to cover boron oxyhydrides. The third area is a theoretical investigation of important intermediates in boron combustion. Structures, thermodynamics and reaction pathways are being studied. All three projects are oriented to assist in the understanding and control of heterogeneous and homogeneous combustion of boron and boron-doped fuels.

TECHNICAL DISCUSSION:

The oxide coating that forms rapidly on boron $(B_2O_3)_n$ has been investigated by fast-atom bombardment mass spectrometry. Bombardment of the glassy surface of oxidized boron by high energy xenon atoms yielded twenty-two gas-phase boron oxide ions that were heretofore unknown.[1,2] Collisional activation of these ions has revealed structural elements that are common to the most stable boron oxide ions. These ions exist with boron limited to two- or three-coordination with oxygen and are thus built upon integral BO_2 triangles and terminal -B=O units.

We have studied the reactions of BH_3 [3] and BH with various oxidants and hydrocarbons. The BH_3 radical is produced by 193nm photolysis of B_2H_6 and monitored by infrared diode laser absorption near 1140 cm^{-1}. The BH is produced by BH_3CO photolysis and probed by UV lif near 430 nm. We have measured rate constants for the reactions of BH_3 with CO, NO and C_2H_4 and upper limits to the rate constants for reaction with O_2 and H_2O. Rate constants for reaction of BH with NO, H_2O, O_2, CO_2, C_2H_4, TME, CO and H_2 have also been measured and will be discussed in the presentation.

Finally, we have been performing ab-initio quantum chemical calculations of potential energy surfaces for species important to boron combustion. Efforts have focussed on the theoretical prediction of heats of formation for small boron hydrides and a few oxygen containing species and on kinetic studies involving critical species.

We have recently completed a theoretical study of the reaction H_2 + BO ---> H + HBO. Our calculations predict this reaction to have a zero point corrected barrier of 9.5 kcal/mole and an exoergicity of 6.4 kcal/mole. The calculated rate constant is well represented over a wide temperature range by the three parameter expression:

$$k(T) = 2.96 \times 10^{-22} T^{3.29} e^{-4.40/RT}$$

We are currently performing a study of the reaction between BO and water. The potential energy

surface calculations are done using multiconfiguration SCF and multireference CI techniques. The rates are computed using conventional or variational transition state theory with quantum corrections along the reaction coordinate. Also underway is the calculation of the regions of the BH_3 potential energy surface important to the unimolecular dissociation to BH and molecular hydrogen.

REFERENCES

1. Doyle, R.J., Jr., Anal. Chem. 1987, 59, 537-539.
2. Doyle, R.J., Jr., J. Am. Chem. Soc. In Press, June 1988 publication.
3. L. Pasternack, R.J. Balla and H.H. Nelson, J. Phys. Chem. 92, 1200 (1988).